Bioresource Technology 160 (2014) 98–106

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Development and evaluation of a new multi-metal binding biosorbent

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HIGHLIGHTS

- The effectiveness of a novel multi-metal binding biosorbent was studied.
- The biosorption of Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} on MMBBs was investigated.
- Equilibrium data were presented and the best fitting models were introduced.
- The pseudo-second order model best describe the biosorption kinetics.
- The obtained results recommend this MMBB as potentially low-cost biosorbent.

ARTICLE INFO

Article history:
Available online 19 December 2013

Keywords:
Agro industrial waste
Biosorption
Heavy metal
Isotherm
Kinetic study

ABSTRACT

A novel multi-metal binding biosorbent (MMBB) was developed by combining a group of three from the selective natural lignocellulosic agro-industrial wastes for effectively eliminating lead, cadmium, copper and zinc from aqueous solutions. Four MMBBs with different combinations (MMBB1: tea waste, corncob, sugarcane bagasse; MMBB2: tea waste, corncob and sawdust; MMBB3: tea waste, corncob and apple peel; MMBB4: tea waste, corncob and grape stalk) were evaluated. FTIR analysis for characterizing the MMBB2 explored that the MMBB2 contains more functional groups available for multi-metals binding. Comparing among the MMBBs as well as the single group biosorbents, MMBB2 was the best biosorbent with the maximum biosorption capacities of 41.48, 39.48, 94.00 and 27.23 mg/g for Cd(II), Cu(II), Pb(II) and Zn(II), respectively. After 5 times of desorption with $CaCl_2$, CH_3COOH and NaCl as eluent, the MMBB2 still remained excellent biosorptive capacity, so as it could be well regenerated for reuse and possible recovery of metals.

1. Introduction

Typical heavy metals such as lead, cadmium, copper and zinc in water and wastewater cause severe disasters in environment and subsequently serious types of acute and chronic diseases in human. The common techniques used for metal removal from water and wastewater includes chemical precipitation, membrane, filtration, ion exchange, carbon adsorption and co-precipitation/adsorption which involve high capital and operational costs and may have secondary wastes after processes (Bilal et al., 2013; Bulut and Tez, 2007).

In recent years, biosorption has been considered as cost effective alternatives for removing metals (Bulut and Tez, 2007; Gupta et al., 2009; Gadd, 2009a; Gadd, 2009b; Volesky, 2007). Generally, biosorption process can reduce capital costs by 20%, operational costs by 36% and total treatment costs by 28% compared with the conventional systems (Loukidou et al., 2004). Thus, the interest in utilization of cheap alternatives has been significantly increased. Many attempts have therefore been made by many researchers on feasibility of biosorption potential of lignocellulosic materials as economic and eco-friendly options, both natural substances and agro-industrial wastes and by-products. These adsorbents may be classified either on basis of their availability (natural materials and industrial/agro-industrial/domestic wastes or by-products and synthesized ones) or depending on their nature (organic and inorganic materials) (Gupta et al., 2009). Among inexpensive biosorbents, most of the studies have been engrossed in lignocellulosic wastes (as naturally intact or chemically modified) such as sawdust, weed and wood waste (Asadi et al., 2008; Bulut and Tez, 2007; Pereira et al., 2010), sugarcane bagasse (Homagai et al., 2010; Martín-Lara et al., 2010; Pereira et al., 2010), fruit rind, pulp and seeds (Feng et al., 2011; Liu et al., 2012; Martín-Lara et al., 2010; Torab-Mostaedi et al., 2013), wheat or barley straw (Pehlivan et al., 2012), rice husk, hull and straw (Asadi et al.,

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http://dx.doi.org/10.1016/j.biortech.2013.12.038

2008; Kazemipour et al., 2008), olive pomace and stone (Blázquez et al., 2009; Martín-Lara et al., 2012), etc. The heavy metal biorecovery can be affected by physico-chemical parameters of the solution such as pH, ion strength, initial metal concentration, temperature and by other characteristics of the adsorbent like concentration, presence of organic and inorganic functional groups and chemical modification (Gupta et al., 2009; Montazer-Rahmati et al., 2011; Pehlivan et al., 2012; Tan and Xiao, 2009; Tan et al., 2010; Velazquez-Jimenez et al., 2013).

The present work is a preliminary study on developing a new multi-metal binding biosorbent (MMBB) by combining a group of high biosorptive capability natural lignocellulosic agro-industrial wastes (e.g., tea waste, corncob, sugarcane bagasse, grape stalk, sawdust, apple peel) to remove cadmium, copper, lead and zinc ions from aqueous solution. These wastes were selected because of the good results reported in other literatures for heavy metal removal. Besides, tea waste, sugarcane, sawdust, apple peel and grape stalk are properly available in Australia and also all over the world.

The effect of pH, contact time, biosorbent dosage and also elution efficiency (sorption and adsorptions cycles) on adsorption capacity were then studied. Finally, the appropriate isotherm and kinetic models were established.

2. Methods

2.1. Preparation of adsorbents and heavy-metal-containing effluent

The stock solution containing Cd, Cu, Pb and Zn were prepared by dissolving cadmium, copper, lead and zinc nitrate salt, $Cd(NO_3)_2.4H_2O$, $Cu_3(NO)_2.3H_2O$, $Pb(NO_3)_2$ and $Zn(NO_3)_2.6H_2O$ in Milli-Q water. All the reagents used for analysis were of analytical reagent grade from Scharlau (Spain) and Chem-Supply Pty Ltd. (Australia). For remove any inaccuracies in metal concentration, all stock solutions were analyzed by AAS (Contra® AA 300, Analytikjena, Germany) to correct their concentration to use in experiments with required amounts.

All biosorbent were bought or collected from local market in Sydney area and after using the useful parts were washed by tap water and distilled water to remove any dirt, color or any impurity and then dried in oven (Labec Laboratory Equipment Pty Ltd., Australia) at 105 °C over night. Having ground and sieved (RETSCH AS-200, Germany) to a particle size of 75–150 μm, the natural biosorbents were kept in desiccator prior to use.

2.2. Biosorption studies in batch system

The tests were performed with synthetic multi-metal solution with concentration of 3000 mg/L for each metal by dilution in Milli-Q water for predetermined metal concentration. The pH of suspensions was adjusted by appropriate amount of HCl and NaOH with concentrations of 0.1 and 1 M. A known weight of adsorbent (5 g/L) was added to a series of 100 mL Erlenmeyer flasks containing 40 mL of metal solution on a shaker (Ratek, Australia) at room temperature and 150 rpm for 3 h. After equilibration, to separate the biomasses from solutions, the solutions were filtered and final concentration of metal was measured using AAS.

2.3. Desorption studies in batch system

Desorption of metal-loaded biosorbent was studied with four types of eluting agents including 0.1 M NaCl, 0.1 M $CaCl_2$, 0.1 M CH_3COOH and milli-Q water. This salts and organic acid were selected for eluting the use biosorbent due to prevent any damages to biosorbent structure. Following biosorption cycle with contact time of 3 h, metal-loaded biosorbent was filtered and then added in 100 ml of above solutions and shaken at 150 rpm for 3 h. After desorption, adsorbent was washed repeatedly with milli-Q water to remove any residual eluting solution and used for the next biosorption cycle.

2.4. Calculations

The amount of heavy metal ion adsorbed, q(mg/g) was calculated from the following Eq. (1):

$$Q = \frac{v(C_i - C_f)}{m} \tag{1}$$

where, C_f and C_i (mg/L) are the initial and equilibrium metal concentrations in the solution, respectively. v (L) the solution volume and m (g) is the mass of biosorbent. All the experiments were carried out in duplicates and the deviation within 5%.

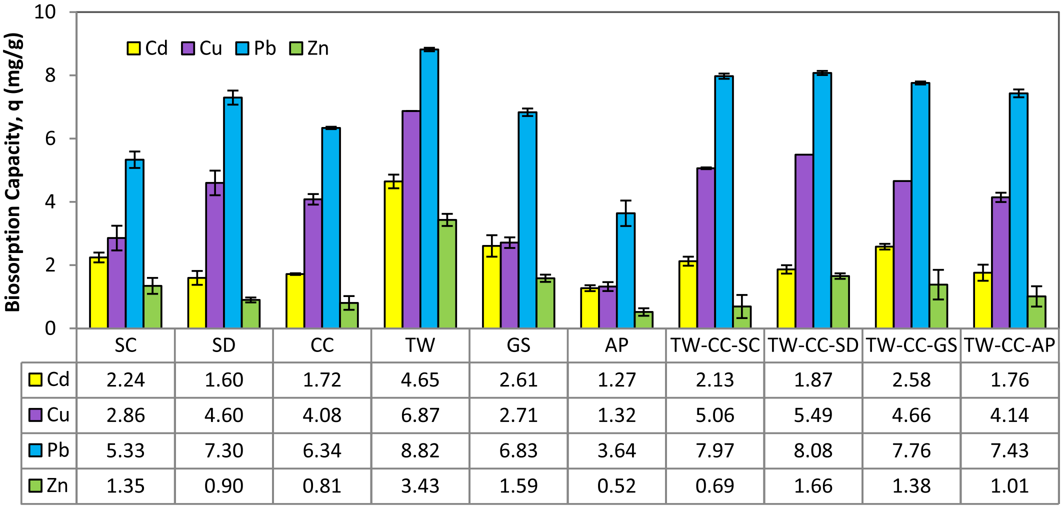
3. Results and discussion

3.1. Selection of adsorbents

Six individual biosorbents, namely, sawdust (SD), sugarcane (SC), corncob (CC) and tea waste (TW), apple peel (AP) and also grape stalk (GS), individually (biosorbent dose: 5 g/L, 50 ppm initial metal Conc. at room temperature and pH of 5.0–5.5, rotary speed of 150 rpm for 24 h) were evaluated and compared in terms of biosorption capacity (Fig. 1). As can be seen in Fig. 1, TW showed the best in removing all tested heavy metal ions (cadmium, copper, lead and zinc) while SC, SD and CC had quite less biosorptive capacity in comparison with GS and TW. AP for Pb, Zn, Cd and Cu removals was very dissatisfactory. Among four MMBBs with different combinations, MMBB2 had highest adsorption capacity of Pb, Cu and Zn (8.08 and 5.49 mg/g, 1.66 mg/g, respectively). However, MMBB2 was not as good as MMBB1 and MMBB3 in terms of Cd removal. Overall, MMBB2 (TW–CC–SD combination) with ratio of 1:1:1 was selected to apply for further experiments. The pH, moisture content (%), loss of mass and bulk density g/cm^3) of MMBB2 were 5.16, 18.63, 0.92 and 0.23, respectively.

3.2. Characterization of adsorbents by FTIR

To determine the functional groups involved in biosorption of Cd(II), Cu(II), Pb(II) and Zn(II) onto MMBB2, a comparison between the FTIR spectra before and after meal loading was done using SHIMADZU FTIR 8400S (Kyoto, Japan). The FTIR spectrum of MMBB2 exhibited a large number of absorption peaks, indicating the complexity in nature of this adsorbent. It also confirmed changes in functional groups and surface properties of MMBB2. The shift of some functional groups bands and their intensity changed because of heavy metal biosorption (Table 1). These shifts may be attributed to carboxylic (C=O) and hydroxylic (O—H) groups on the MMBB2's surface. They were dominantly active groups in Cd(II), Cu(II), Pb(II) and Zn(II) biosorption process, suggesting that acidic groups, carboxyl and hydroxyl, are main contributors in the complexation of metal cations and ion exchange processes. Amine and amide groups were found between medium intensity peaks in the frequency range of 3400–3250 with 4.9 cm^{-1} shift after biosorption process. The strong peaks detected in spectra were lied between 1320–1000 and 1820–1680 cm^{-1} which are related to C—O stretch (COOH) and C=O stretch in amides, ketones, aldehydes, carboxylic acids and esters, respectively (Feng et al., 2011; Hossain et al., 2012).



	SC	SD	CC	TW	GS	AP	TW-CC-SC	TW-CC-SD	TW-CC-GS	TW-CC-AP
🟨 Cd	2.24	1.60	1.72	4.65	2.61	1.27	2.13	1.87	2.58	1.76
🟪 Cu	2.86	4.60	4.08	6.87	2.71	1.32	5.06	5.49	4.66	4.14
🟦 Pb	5.33	7.30	6.34	8.82	6.83	3.64	7.97	8.08	7.76	7.43
🟩 Zn	1.35	0.90	0.81	3.43	1.59	0.52	0.69	1.66	1.38	1.01

Fig. 1. Comparison between different single and multi-metal binding biosorbent for Cd(II), Cu(II), Pb(II) and Zn(II) adsorption (initial pH 5.5 ± 0.1; room temperature, 22 ± 2 °C; contact time: 24 h; initial metal conc.: 50 mg/L; biosorbent dose: 5 g/L; rotary speed: 150 rpm, particle size: 75–150 μm) SC: Sugarcane, SD: Sawdust, CC: Corncob, TW: Tea Waste, GS: Grape Stalk and AP: Apple Peels.

Table 1
FTIR spectra of unloaded and metal loaded-biosorbents.

Wavelength range (cm^{-1})		Transmittance (%)			Bond/functional group
Frequency	Difference	Unloaded	Loaded	Difference	
3500–3200	−8.3	71.8	64.4	−7.4	O—H stretch/alcohols and phenols
3400–3250	−4.9	64.5	53.5	−11.0	N—H band/1° and 2° amines and amides
3000–2850	−10.4	73.2	65.7	−7.5	H—C—H asymmetric and symmetric stretch/alkanes
1820–1680	−9.1	69.3	64.3	−5.0	C═O stretch/amides, ketones, aldehydes, carboxylic acids and esters
1470–1450	−3.6	62.7	61.1	−1.7	C—H band/alkanes
1550–1475	+6.0	72.3	65.5	−6.8	N—O asymmetric stretch/nitro compounds
1320–1000	−9.3	79.1	68.5	−10.6	C—O stretch (COOH)/alcohol, carboxylic acid, esters and ethers

Moreover, a big change occurred on the biosorbent after metal loading which is reflected in the strong and broad band present between 3500–3200 cm^{-1}. This may be assigned to complexation of metal ions with the ionized O—H groups of polymeric compounds such as alcohols, phenols and carboxylic acids of cellulose and lignin of lignocellulosic materials (Feng et al., 2011; Hossain et al., 2012).

The changes of peaks in the range of 3000–2850 and 1470–1450 cm^{-1} indicated the involvement of H—C—H asymmetric and symmetric stretch and C—H stretch of alkanes, respectively which can be found in the molecular structure of MMBB2.

3.3. Effect of different physico-chemical parameters

3.3.1. Influence of pH

The adsorption of cadmium, copper, lead and zinc was studied as a function of pH altering in the range of 2.0−5.5 ± 0.1. At initial pH values of 6.0, lead and copper hydroxide precipitation occurred. Thus, the experiments were not conducted beyond pH 5.5 to avoid any precipitation. Fig. 2 shows that the adsorption capacity of metals increased with increasing in pH values in all cases. However, the changes of Cu and Pb adsorption was much more obvious than that of Zn and Cd (e.g., Cu; 1.07–5.70 mg/g, Pb: 2.50–8.53 mg/g, Zn: 0.29–1.83 mg/g and Cd: 1.30–1.72 mg/g). In addition some metal ions have better affinity towards biosorbents than other ions and this fact ascertains the selectivity potential of functional group (Šćiban et al., 2007). This phenomenon can be confirmed later by calculating the Langmuir parameter of b_L representing this attraction.

3.3.2. Influence of contact time

A series of contact time experiments for cadmium, copper, lead and zinc adsorption on MMBB2 from 0 to 24 h were carried out at 50 mg/L initial concentration and room temperature. It is evident from the Fig. 3 that the rate of metal uptake was very fast within first 30 min as a result of exuberant number of available active sites on adsorbent surface and the process reached the equilibrium state within approximately 180 min of contact time for all cases.

3.3.3. Influence of adsorbent dose

As shown in Fig. 4, there is a hike in removal efficiency of all heavy metal ions on MMBB2 when adsorbent dose increased and after 5 g/L of adsorbent dose. As it plateaued, the optimum amount of adsorbent for future study would be 5 g/L whose highest removal efficiencies were about 68%, 75%, 85% and 55% for Cd, Cu, Pb and Zn, respectively.

3.3.4. Sorption and desorption experiments

The ability of biosorbent regeneration and batch sorption and desorption studies were conducted using four eluting agents (0.1 M NaCl, 0.1 M $CaCl_2$, 0.1 M CH_3COOH and Milli-Q water). The biosorption capacity of eluted biosorbent was tested in five repeated cycles at optimum pH 5.5 ± 0.1 and 50 mg/L initial metal concentrations. The contact time was 3 h for sorption and desorption in each cycle. The biosorption capacity of MMBB2 for Cd(II), Cu(II), Pb(II) and Zn(II) removal in the five cycles are indicated in Fig. 5. To evaluate level of significance in the sorption and desorption cycles on the biosorption capacity, SPSS software was used for statistical testing of the model in the form of analysis of variance

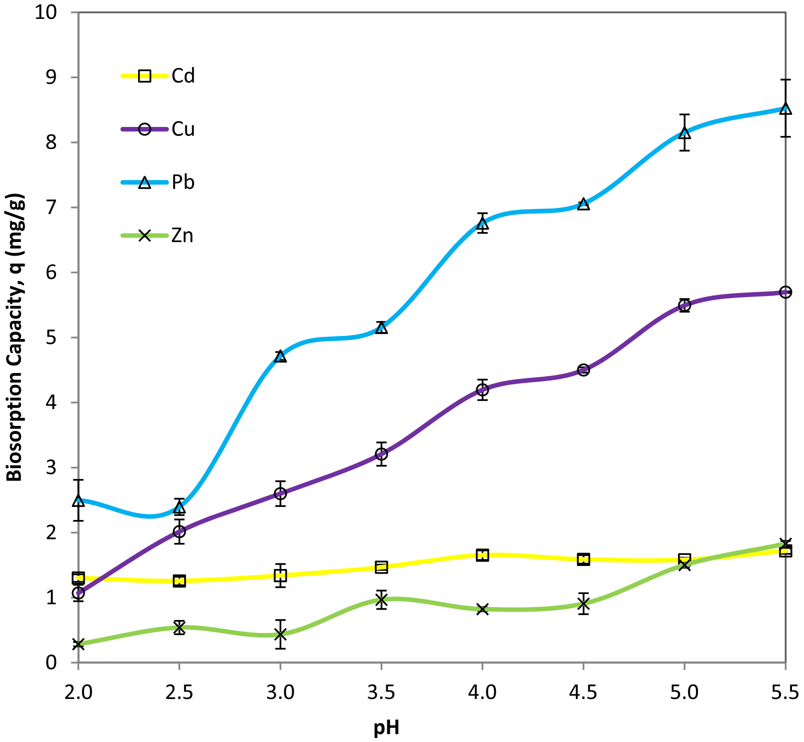


Fig. 2. Effect of initial pH of solution on Cd(II), Cu(II), Pb(II) and Zn(II) adsorption (room temperature, 22 ± 2 °C; contact time: 24 h; initial metal conc.: 50 mg/L; biosorbent dose: 5 g/L; rotary speed: 150 rpm, particle size: 75–150 μm).

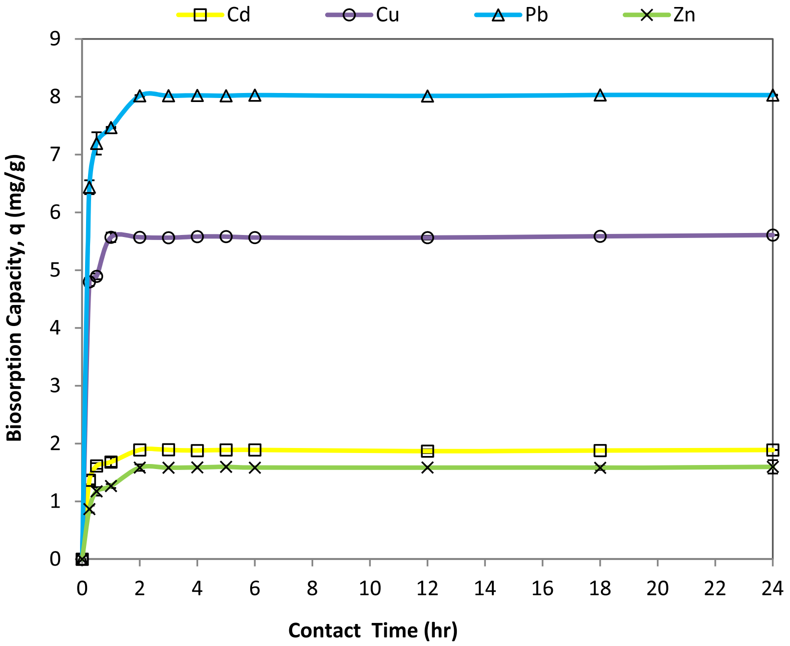


Fig. 3. Effect of contact time on Cd(II), Cu(II), Pb(II) and Zn(II) adsorption (pH 5.5 ± 0.1; room temperature, 22 ± 2 °C; initial metal conc.: 50 mg/L; biosorbent dose: 5 g/L; rotary speed: 150 rpm, particle size: 75–150 μm).

(ANOVA) and the one-sample *t*-test were done. For a 5% level of significance, the ANOVA data are given in Table 2. From this table for all metals, *P* value is less than 0.05 and also the values of *F* are higher than the critical *F*. Therefore, the type of eluent affects the sorption capacity and there is significant difference between the four desorbing agents in Cd(II), Cu(II), Pb(II) and Zn(II) removal. In this case, a *P* value less than 0.05 would result in the rejection of the null hypothesis at the 5% (significance) level.

For a 5% level of significance *T* values for NaCl, CH_3COOH and $CaCl_2$, for all Zn(II) and Cd(II), the *P* value is higher than 0.05 and also the values of *T* are lower than the critical *T* (2.13). In other word, it is obvious from the *t*-tests that for these eluents, the num-

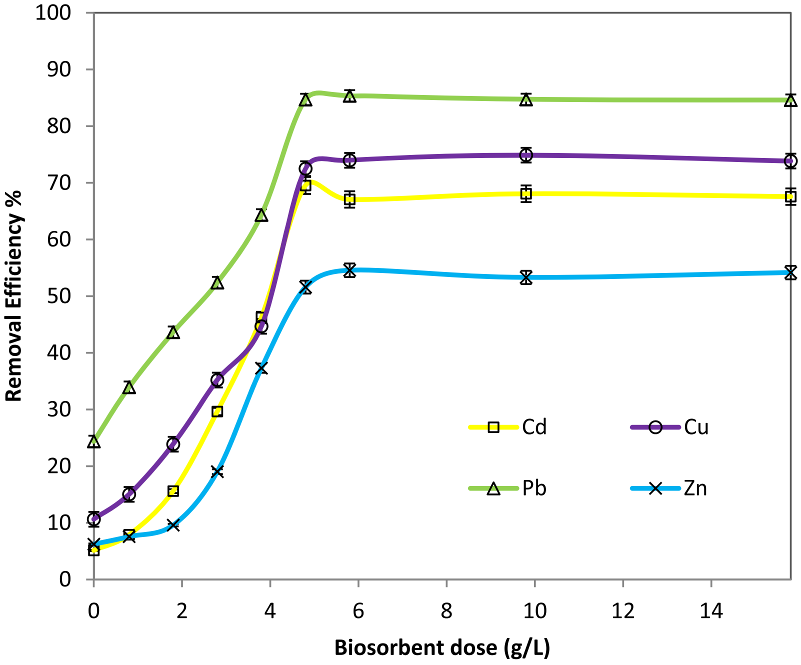
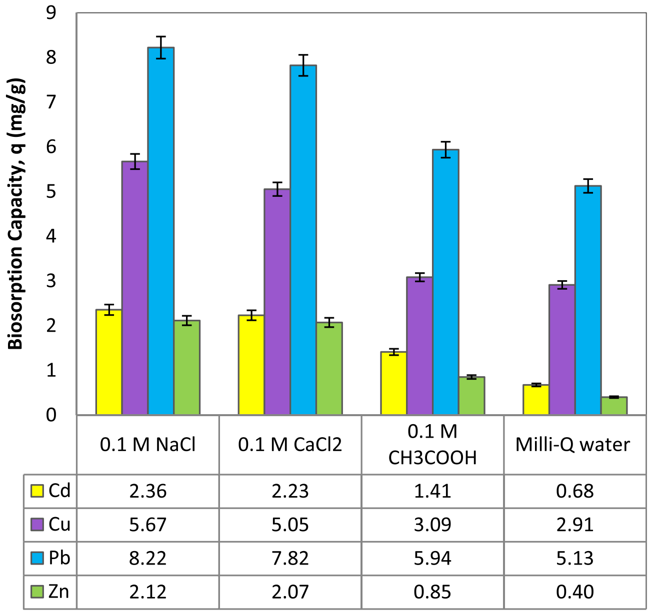


Fig. 4. Effect of biosorbent dose on Cd(II), Cu(II), Pb(II) and Zn(II) adsorption (initial pH 5.5 ± 0.1, room temperature, initial metal conc.: 50 mg/L, contact time: 3 h, rotary speed: 150 rpm, particle size: 75–150 μm).



	0.1 M NaCl	0.1 M CaCl2	0.1 M CH3COOH	Milli-Q water
🟨 Cd	2.36	2.23	1.41	0.68
🟪 Cu	5.67	5.05	3.09	2.91
🟦 Pb	8.22	7.82	5.94	5.13
🟩 Zn	2.12	2.07	0.85	0.40

Fig. 5. Biosorption capacity of Cd(II), Cu(II), Pb(II) and Zn(II) onto MMBB2 washed by four eluting agents (optimum pH 5.5 ± 0.1; room temperature: 22 ± 2 °C; sorption time: 3 h; desorption time: 3 h; 5 cycles; initial metal conc.: 50 mg/L).

Table 2
ANOVA and One sample *t*-test data for sorption and desorption experiments of Cd(II), Cu(II), Pb(II) and Zn(II) biosorption onto MMBB2 (optimum pH 5.5 ± 0.1; room temperature: 22 ± 2 °C; sorption time: 3 h; desorption time: 3 h; 5 cycles; initial metal conc.: 50 mg/L).

Statistical analysis method	Metal			
	Cd	Cu	Pb	Zn
One-way ANOVA for NaCl, $CaCl_2$, CH_3COOH and Milli-Q water				
F factor	12.23	4.66	4.86	4.59
$F_{critical}$ factor	3.23	3.23	3.23	3.23
P value	0.0002	0.0158	0.0136	0.0166
One–sample T for NaCl				
T factor	2.31	4.08	4.66	0.02
$T_{critical}$ factor	2.13	2.13	2.13	2.13
P	0.04	0.007	0.004	0.49
One–sample T for $CaCl_2$				
T factor	0.64	4.92	4.47	1.19
$T_{critical}$ factor	2.13	2.13	2.13	2.13
P	0.27	0.004	0.005	0.15
One–sample T for CH_3COOH				
T factor	1.93	7.16	5.19	2.81
$T_{critical}$ factor	2.13	2.13	2.13	2.13
P	0.06	0.001	0.003	0.02
One–sample T for Milli-Q water				
T factor	5.00	5.60	4.76	5.48
$T_{critical}$ factor	2.13	2.13	2.13	2.13
P	0.003	0.02	0.004	0.005

ber of elution times does not affect the biosorption process. However, biosorption results show that the effect of $CaCl_2$ and NaCl on the biosorbent is significant and causes higher increase in the sorption capacity in comparison with CH_3COOH and Milli-Q water. Hence, these two chemicals are recommended as elution agents and desorption of cadmium, copper, lead and zinc from the biosorbent. Of course the much lower cost of NaCl should also be taken into consideration.

3.4. SEM analysis

Scanning Electron Microscopy (SEM) of the free and loaded biomass of TMM and MMBB2 was performed on ZEISS EVO|LS15 (Germany) at an accelerating voltage of 10 kV and with the working distance of 10–100 μm for MMBB2 to elucidate the porous properties of the biosorbents. SEM images exhibited the morphological changes on the biosorbent surface before and after metal biosorption as well as 5 cycle of sorption and desorption. The surface of natural MMBB2 was found to be more porous and rougher than that of metal-loaded biosorbent. It was also observed that after 5 cycles of sorption and desorption, the surface of MMBB2 remained as rough as that of biosorbent after only one sorption process.

3.5. Adsorption kinetics

In batch systems, the adsorption kinetics was described by a number of models with varying degrees of complexity such as pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic model. The pseudo-first-order kinetic model known as the Lagergren equation and takes the form as (Febrianto et al., 2009):

$$q_t = q_e[1 - \exp(-K_1 t)] \tag{2}$$

where, q_t and q_e are the metal adsorbed at time t and equilibrium, respectively, and K_1 (min^{-1}) is the first-order reaction rate equilibrium constant.

The pseudo-second-order kinetic model considered in this study is as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{qe} \tag{3}$$

where, K_2 ($\mathrm{g\ mg^{-1}\ min^{-1}}$) is the second-order reaction rate equilibrium constant.

The intra-particle diffusion model follows:

$$q_t = K_p t^{1/2} + C \tag{4}$$

The experimental data and obtained parameters of these models were measured by MATLAB® and shown in Table 3. The results indicate that pseudo-second-order kinetic model can describe experimental data better than the two other kinetic models ($R^2 = 0.99$), suggesting that chemical reaction would be presumably the rate limiting step of Cd, Cu, Pb and Zn biosorption on MMBB2. The calculated value of q_e for pseudo-second-order kinetic model (1.92, 5.88, 8.06 and 1.60 mg/g for Cd(II), Cu(II), Pb(II) and Zn(II), respectively) are also close to the experimental values (1.89, 5.57, 8.04 and 1.60 mg/g).

3.6. Adsorption isotherm

To optimize the design of biosorption process, it is necessary to acquire the appropriate correlation for equilibrium curve. In this study, the metal biosorption capacity as a function of metal concentration (1–500 mg/g) at equilibrium state has been described by very common two-parameter models of Langmuir, Freundlich, Dubinin–Radushkevich and Temkin and three-parameter models of Sips, Redlich–Peterson and Radke–Prausnitz adsorption isotherms. All the model parameters were evaluated by non-linear regression using MATLAB® software. Furthermore, residual root mean square error (RMSE), error sum of square (SSE) and coefficient of determination (R^2) were used to measure the goodness of fitting along with model parameters.

Langmuir isotherm model is as follows:

$$q_e = \frac{q_{m,L} b_L C_e}{1 + b_L C_e} \tag{5}$$

where, $q_{m,L}$ is the maximum metal biosorption and b_L (L/mg) the Langmuir constant. These constants related to monolayer adsorption capacity and energy of adsorption, respectively (Tan et al., 2010). Maximum monolayer adsorption capacities ($q_{m,L}$) were 41.48, 39.48, 94.00 and 27.23 mg/g for Cd(II), Cu(II), Pb(II) and Zn(II) sorption, respectively. The b values of Cd(II), Cu(II), Pb(II) and Zn(II) biosorption which were estimated from this isotherm are 0.001, 0.004, 0.007 and 0.002 L/mg, respectively and shows the steepest initial isotherm slope (the highest b_L) is for Pb(II) as can be expected.

Freundlich isotherm model is an empirical equation presented as follows (Montazer-Rahmati et al., 2011):

$$q_e = K_F C_e^{1/n} \tag{6}$$

where K_F (L/g) is Freundlich constant and n the Freundlich exponent. It is assumed that the stronger binding sites on a heterogeneous surface are occupied first and binding strength decreases with increasing degree of site occupation.

From Table 4(a), it is apparent that equilibrium data of Cd(II), Cu(II) and Pb(II) biosorption fitted well by the Freundlich isotherm ($R^2 = 0.99$) and for Zn(II) the Langmuir isotherm was quite better fitted than Freundlich isotherm according to the values of R^2 of Langmuir isotherm model (0.97) being higher than that of Freundlich isotherm (0.95) as well as values of RMSE and SSE which are quite less than those of the other three models. Besides, it was understood that the Langmuir isotherm corresponded to a dominant ion exchange mechanism while the Freundlich isotherm showed adsorption–complexation reactions taking place in the adsorption process (Asadi et al., 2008).

The Dubinin–Radushkevich (D–R) equation is generally expressed as follows:

$$q_e = q_{\mathrm{D-R}} \exp(-B_{\mathrm{D-R}} \epsilon_{\mathrm{D-R}}^2) \tag{7}$$

$$\epsilon_{\mathrm{D-R}} = \mathrm{RT}\ \ln\left(1 + \frac{1}{C_e}\right) \tag{8}$$

Where $\varepsilon_{\mathrm{D-R}}$, the Polanyi potential, is a constant related to the biosorption energy, R is the gas constant (8.314 kJ/mol) and T is the absolute temperature (K). $q_{\mathrm{D-R}}$ and $B_{\mathrm{D-R}}$ are the D–R isotherm constants in mg/g and $\mathrm{mol^2/kJ^2}$, respectively. Moreover, the mean free energy of adsorption $\left(E = \frac{1}{\sqrt{2B_{\mathrm{D-R}}}}\right)$ calculated from Dubinin–

Table 3
Comparison between adsorption rate constants, the estimated q_e and the coefficients of determination associated with the *Lagergren* pseudo-first-order, the pseudo-second order and intra-particle diffusion kinetic models (pH 5.5 ± 0.1; room temperature, 22 ± 2 °C; initial metal conc.: 50 mg/L; biosorbent dose: 5 g/L; rotary speed: 150 rpm, particle size: 75–150 μm).

Model	Parameter	Metal			
		Cd	Cu	Pb	Zn
Experimental	$q_{e,\exp}$ (mg/g)	1.89	5.57	8.04	1.60
1st-order kinetic model $q_t = q_e[1 - \exp(-K_1 t)]$	K_1 (min^{-1})	0.03	0.10	0.07	0.02
	$q_{e,\mathrm{cal}}$ (mg/g)	1.19	5.98	8.39	1.21
	R^2	0.79	0.95	0.94	0.85
2nd-order kinetic model $\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$	$K_2 \times 10^3$ ($\mathrm{g\ mg^{-1}\ min^{-1}}$)	0.17	0.08	0.06	0.09
	$q_{e,\mathrm{cal}}$ (mg/g)	1.92	5.88	8.06	1.60
	R^2	0.99	0.99	0.99	0.99
Intra-particle diffusion model $q_t = K_P t^{0.5} + C$	K_P ($\mathrm{mg\ g^{-1}\ min^{-0.5}}$)	0.07	1.12	0.15	0.07
	C	1.16	4.35	6.19	0.68
	R^2	0.93	0.81	0.88	0.90

Table 4
Isotherm constants of (a) two-parameter and (b) three-parameter models for Cd(II), Cu(II), Pb(II) and Zn(II) adsorption (initial pH 5.5 ± 0.1, initial metal Conc.: 1–500 mg/L, contact time: 3 h, rotary speed: 150 rpm, biosorbent dose: 5 g/L, particle size: 75–150 μm).

	Metal			
	Cadmium	Copper	Lead	Zinc
(a) *Two-parameter models*				
Langmuir $q_e = \frac{q_{m,L} b_L C_e}{1+b_L C_e}$				
$q_{m,L}$(mg/g)	41.48	39.48	94.00	27.23
b_L (L/mg)	0.001	0.004	0.007	0.002
SSE	2.24	4.52	65.03	3.89
R^2	0.99	0.99	0.97	0.97
RMSE	0.75	1.06	4.03	0.98
Freundlich $q_e = K_F C_e^{1/n}$				
K_F	0.21	0.63	2.57	0.18
n	1.37	1.63	1.74	1.42
SSE	1.83	0.27	12.71	6.65
R^2	0.99	0.99	0.99	0.95
RMSE	0.67	0.25	1.78	1.29
Dubinin–Radushkevich $q_e = q_{\mathrm{D-R}} \exp(-B_{\mathrm{D-R}} \epsilon_{D-R}^2)$				
$q_{\mathrm{D-R}}$ (mg/g)	18.00	21.68	47.99	14.56
$B_{\mathrm{D-R}}$	0.008	0.005	0.004	0.018
SSE	18.54	59.54	40.60	6.50
R^2	0.91	0.83	0.81	0.96
RMSE	2.15	3.85	10.07	1.27
Temkin $q_e = \frac{RT}{b_{\mathrm{Te}}} \ln (K_{\mathrm{Te}} C_e)$				
K_{Te} (L/g)	0.15	0.21	1.16	0.08
b_{Te} (kJ/mol)	0.77	0.55	0.31	0.77
SSE	50.17	56.4	42.34	26.89
R^2	0.75	0.84	0.80	0.82
RMSE	3.54	3.75	10.29	2.59
(b) *Three-parameter models*				
Radke–Prausnitz $q_e = \frac{a_{\mathrm{R-P}} r_{\mathrm{R-P}} C_e^{\beta_{\mathrm{R-P}}}}{a_{\mathrm{R-P}} + r_{\mathrm{R-P}} C_e^{\beta_{\mathrm{R-P}-1}}}$				
$a_{\mathrm{R-P}}$ (L/g)	5.10	9.24	3.25	4.10
$\beta_{\mathrm{R-P}}$	0.68	0.61	0.57	0.70
$r_{\mathrm{R-P}}$ (L/mg)	0.21	0.63	2.57	0.18
SSE	1.33	0.26	12.71	6.65
R^2	0.99	0.99	0.99	0.95
RMSE	1.52	0.99	2.05	1.48
Redlich–Peterson $q_e = \frac{K_{\mathrm{RP}} C_e}{1+a_{\mathrm{RP}} C_e^{\beta_{\mathrm{RP}}}}$				
a_{RP}(L/mg)	1.25	0.10	2.09	5.39
β_{RP}	0.27	0.60	0.19	0.56
K_{RP} (L/g)	5.65	0.89	1.00	0.05
SSE	1.83	6.77	0.23	2.87
R^2	0.99	0.99	0.99	0.98
RMSE	0.78	4.75	0.27	0.97
Sips $q_e = \frac{K_S C_e^{\beta_S}}{1+a_S C_e^{\beta_S}}$				
a_S (L/mg)	0.001	0.004	0.063	0.001
β_S	0.83	0.59	0.38	1.72
K_S (L/g)	0.20	0.66	3.68	0.002
SSE	1.52	0.25	2.92	1.89
R^2	0.99	0.99	0.99	0.98
RMSE	0.23	0.29	0.98	0.79

Radushkevich isotherm which is applied to evaluate sorption properties and indicates if main mechanism is chemical reaction dominated by ion exchange or physical adsorption. Based on hypothesis of D–R isotherm, E values between 8 and 12 kJ/mol mean chemical adsorption by ion exchange process whereas E values less than 8 kJ/mol means physical adsorption. Hence, according to calculated $B_{\mathrm{D-R}}$ for Cd, Cu, Pb and Zn, E values show physical adsorption for cadmium and zinc removal (7.81 and 5.27 kJ/mol, for Cd and Zn, respectively) and ion-exchange process for lead and copper biosorption (9.45 kJ/mol for Cu and 10.54 kJ/mol for Pb).

According to Temkin isotherm, interactions between adsorbate and adsorbent make linear decrease in adsorption energy and heat of adsorption. The model is mathematically represented as (Febrianto et al., 2009):

$$q_e = \frac{\mathrm{RT}}{b_{\mathrm{Te}}} \ln (K_{\mathrm{Te}} C_e) \tag{9}$$

where b_{Te} (kJ/mol) and K_{Te} (L/g) are Temkin model constants which are 0.77, 0.55, 0.31 and 0.77 kJ/mol and 0.15, 0.21, 1.16 and 0.08 L/g, for for Cd(II), Cu(II), Pb(II) and Zn(II), respectively. This model is not a proper correlation for examined heavy metals according to R^2, RMSE and SSE values.

Radke–Prausnitz isotherm can be represented as (Montazer-Rahmati et al., 2011):

$$q_e = \frac{a_{\mathrm{R-P}} r_{\mathrm{R-P}} C_e^{\beta_{\mathrm{R-P}}}}{a_{\mathrm{R-P}} + r_{\mathrm{R-P}} C_e^{\beta_{\mathrm{R-P}-1}}} \tag{10}$$

Table 5
Biosorption capacities of various biosorbent.

Adsorbent	Matal	q_{max}(mg/g)	References
MMBB2	Cd(II)	41.48	Present study
	Zn (II)	27.23	
	Pb(II)	94.00	
	Cu (II)	39.48	
Sugarcane bagasse	Cd(II)	69.06	Garg et al. (2008)
Sawdust	Cu(II)	6.88	Šćiban et al. (2007)
	Zn(II)	0.96	
	Cd(II)	0.15	
Rice straw	Cd(II)	13.89	Ding et al. (2012)
Olive stone	Pb(II)	92.6	Fiol et al. (2006)
	Cd(II)	77.3	
	Ni(II)	21.3	
	Cu(II)	20.2	Feng et al. (2011)
Orange peel	Pb(II)	113.5	
	Cd(II)	63.35	
	Ni(II)	9.82	
Cashew nut shell	Zn(II)	24.98	Kumar et al. (2012)
Tea waste	Cu(II)	48	Amarasinghe and Williams (2007)
	Pb(II)	65	

where a_{R-P} and r_{R-P} are Radke–Prausnitz model constants and β_{R-P} the Radke–Prausnitz model exponent. Radke–Prausnitz isotherm constants, a_{R-P} and r_{R-P} for Cd(II), Cu(II), Pb(II) and Zn(II) were calculated as 5.10, 9.24, 3.25 and 4.10 L/mg, 0.21, 0.63, 2.57 and 0.18 L/g, respectively.

As the results in Table 4(a), among two-parameter isotherms, both Freundlich and Langmuir models agreed very well with experimental data rather than the other two-parameter isotherm models and these are confirmed by small values of RMSE and SSE and R^2 amounts closed to 1.0, too. This result indicates the formation of monolayer coverage of metal ions at the outer heterogeneous surface of the sorbent.

The Sips isotherm is a combination of the Langmuir and Freundlich isotherm models and is expected to describe heterogeneous surfaces much better. At high sorbate concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm whereas at low sorbate concentrations it reduces to the Freundlich isotherm. It is given as (Febrianto et al., 2009):

$$q_e = \frac{K_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}} \tag{11}$$

where K_S and a_S are the Sips model constants in L/g and L/mg, respectively and β_S is the Sips model exponent.

As the results given by Sips model (Table 4(b)), the experimental results of Cd(II), Cu(II) and Zn(II) biosorption are well fitted by all Sips better than Redlich–Peterson and Radke–Prausnitz models due to small RMSE and SSE as well as high R^2 close to 1.0.

Unlike Sips model, the Redlich–Peterson isotherm behaves like the Freundlich isotherm at high adsorbate concentrations and comes close the Henry's law at low amounts of concentration. The model can be presented as (Febrianto et al., 2009; Montazer-Rahmati et al., 2011):

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{\beta_{RP}}} \tag{12}$$

where K_{RP} and a_{RP} are the Redlich–Peterson model constants in L/g and L/mg, respectively and β_{RP} is the Redlich–Peterson model exponent which lies between 0 and 1 (0.27, 0.60, 0.19 and 0.56 for Cd(II), Cu(II), Pb(II) and Zn(II), respectively). Pb(II) biosorption data is best correlated by the Redlich–Peterson as confirmed by the smallest values of RMSE, SSE and R^2 values very close to 1.0 (0.999).

The foregoing analysis of isotherm models show that the best fit for Cd(II), Cu(II), Pb(II) and Zn(II) biosorption is produced by three-parameter isotherm models than two-parameter isotherm models.

Comparison between maximum adsorptive capacities of some adsorbents investigated by other researchers is shown in Table 5. This study results are compatible with other adsorbents by higher or at least equal sorptive potential for heavy metal removal from aqueous solutions. Besides, combination of several types of low-cost agro-industrial waste provides more selectivity as a result of increase in different effective functional groups involved in metal binding. Hence, this kind of adsorbent will be recommended for its significant advantages.

4. Conclusion

The new biosorbent containing tea waste, corncob and sawdust was found to be an effective and low-cost alternative for detoxifying of heavy metals contaminated aqueous solutions. The pH, contact time, adsorbent dose and initial metal concentrations of the adsorbate significantly governed the overall process of cadmium, copper, lead and zinc cations adsorption. The sorption equilibrium time was reached within 3 h and pseudo-second-order kinetic model well fitted the experimental data. NaCl was successfully used as eluent without affecting its sorption capability after five cycles of sorption and desorption.

Acknowledgement

This work was supported by Centre for Technology in Water and Wastewater (CTWW), School of Civil and Environmental Engineering, University of Technology, Sydney (UTS) and Australian Postgraduate Award (APA).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2013.12.038.

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